Characterization Studies on Li-Metal Anode and High-Ni Cathode Materials

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BATTERY 500 CONSORTIUM

BROOKHAVEN NATIONAL LABORATORY

Overview

Timeline

- Project start date: 10/01/2016
- Project end date: 9/30/2021
- Percent complete: 70 percent

Budget

Total project funding: DOE share $50M

Funding received in FY 2019: $10M

Funding for FY 2020: $10M

Barriers addressed

- Develop Li-ion batteries using Li metal anodes with a cell-level energy density of 500 Wh/kg
- Achieve lifetime of 1,000 cycles with the technology
- Mitigate safety issues associated with Li metal

Collaborators

- Argonne National Laboratory (ANL)
- Idaho National Laboratory (INL)
- Pacific Northwestern National Laboratory (PNNL)
- Stanford Linear Accelerator Center (SLAC)
- Binghamton University
- University of Texas - Austin
- University of Maryland – College Park
- University of California San Diego (UCSD)

Relevance and Project Objectives

- Accelerate development of 500 Wh/kg batteries with Li metal anodes
- Develop and deploy characterization techniques to:
  1. Select and optimize high energy density cathode materials
  2. Diagnose failure mechanisms with spatial and temporal resolution
  3. Parameterize & validate whole-cell models, leading to improved cell designs
- Emphasis on synchrotron diffraction and spectroscopy methods
  - Done both locally at BNL and externally at other DOE facilities

Milestones

Month/Year	Milestones
Dec/2019	Complete x-ray pair distribution function (PDF) studies on high sulfur loading S cathode material synthesized by carbonizing the oxygen-rich PTCDA and nitrogen-rich PAN with sulfur to understand the mechanism of high S loading and cycleability of this new material. (Q1, December 2019) ➥ *Completed.*
Mar/2020	Complete transmission x-ray microscopy (TXM) 3D tomography studies of high Ni content cathode material ($LiNi_{0.94}Co_{0.06}O_2$ NC9406) after multiple cycles to different charge limits. Comparing the results with those from $LiNi_{0.94}Co_{0.06}O_2$ NC9406 to diagnose the failure mechanism of this material. (Q2, March 2020) ➥ *Completed.*
Jun/2020	Complete transmission x-ray microscopy (TXM) 3D tomography studies of Al-doped high Ni content cathode material ($LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$ NCA920602) after multiple cycles to different charge limits. Comparing the results with those from $LiNi_{0.94}Co_{0.06}O_2$ NC9406 to understand the effects of Al doping. (Q3, June 2020) ➥ *On schedule.*
Sep/2020	Complete studies of spatially-resolved X-ray diffraction studies of Li-S pouch cell in order to understand the inhomogeneity of electrochemical reactions and its effects on fade and failure mechanism of Li-S cells during cycling. (Q4, September 2020) ➥ *On schedule.*

Approach – methods

- Develop and apply **multi-scale** and **multi-dimensional** techniques
- **Multi-scale:**
  - Apply both <u>bulk</u> (XRD, PDF) and <u>single-particle</u> (TEM, TXM) probes
  - Study both the <u>average structure</u> and <u>local structure</u> of cathode materials
- **Multi-dimensional:**
  - 1D depth-profiling thick film *operando* studies of time-dependent SOC
  - 2D lateral mapping film / full pouch cell studies done *ex situ* or *in operando*
  - 3D tomographic studies of single particles done *ex situ*

Approach – goals

1. **Select and optimize materials**

    1a. High-precision quantification of anti-site defects in NMCs

    1b. PDF studies of carbon-sulfur hybrids

2. **Diagnose failure mechanisms with spatial and temporal resolution**

    2a. Pouch cell failure probed through lateral mapping studies

    2b. Particle-level failure probed through TXM tomography

    2c. Material-level failure probed using super-resolution electron microscopy

3. **Parameterize and validate whole-cell models**

    3a. Depth profiling studies of thick cathode films

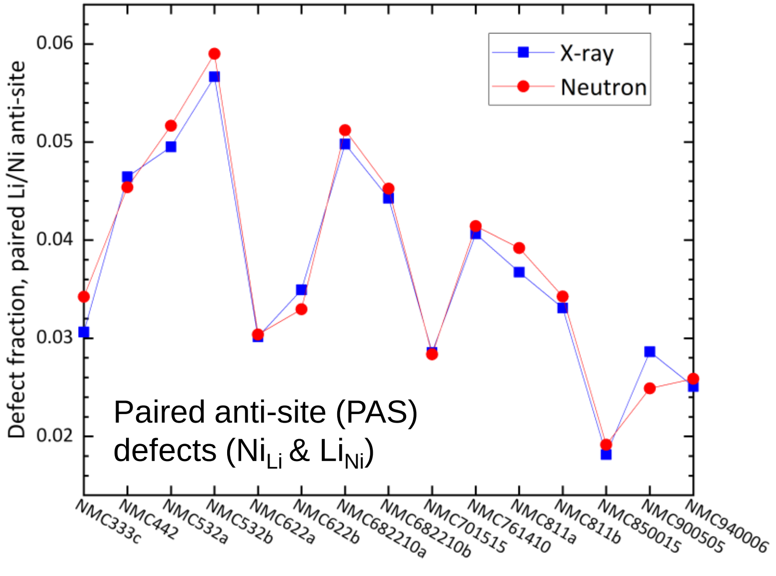
Technical accomplishments – highlights

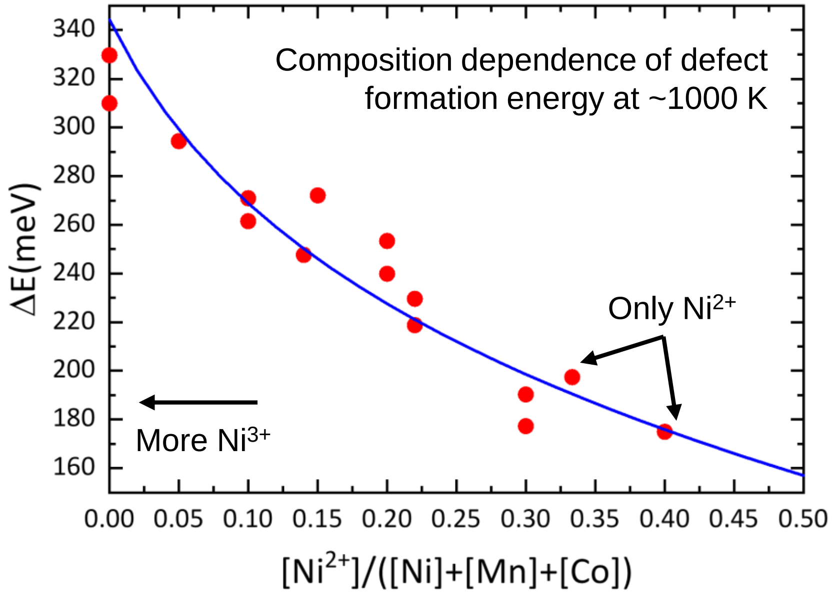
- XRD quantification of defects in NMC cathodes with unprecedented accuracy
- Demonstrated ability of PDF methods to resolve non-crystalline S coordination

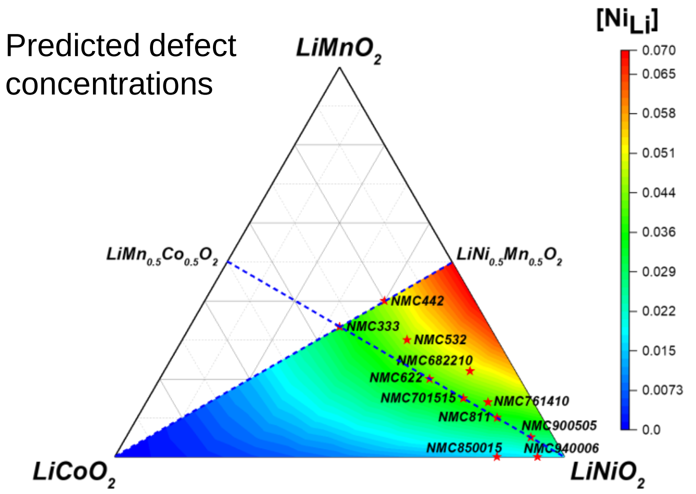
- Developed high-throughput lateral mapping to study pouch cell failure signatures
- 3D SOC maps of NMC single particles to understand failure mechanism
- Used ML to rapidly identify defects in EM images with exceptional sensitivity

- Measured and modeled SOC gradients in thick NMC films

1a. Precise XRD quantification of NMC defects





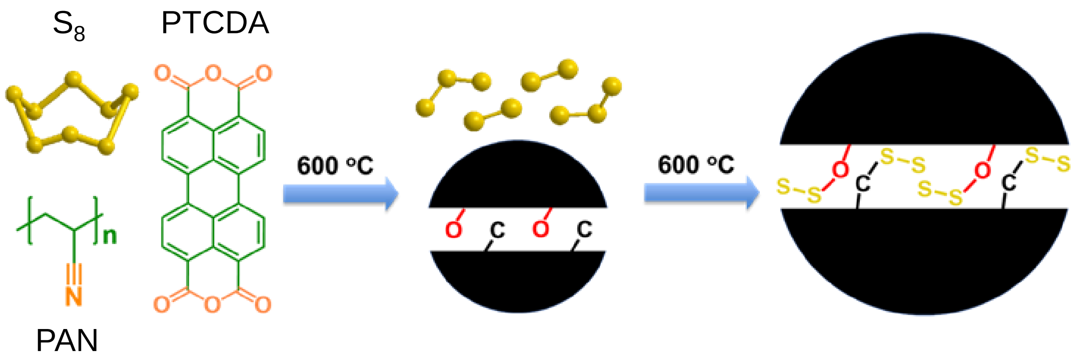


- Developed and validated new diffraction methods for defect quantification at ppt levels
  - Accuracy unprecedented in history of powder diffraction; exceeds sensitivity of chemical analysis
- Enabled calculation of defect formation energy and prediction of defect concentrations
  - Defect formation shown to be driven not just by Ni^{2+} size, but by TM layer expansion
- Now possible to determine optimal defect concentration for cycling performance

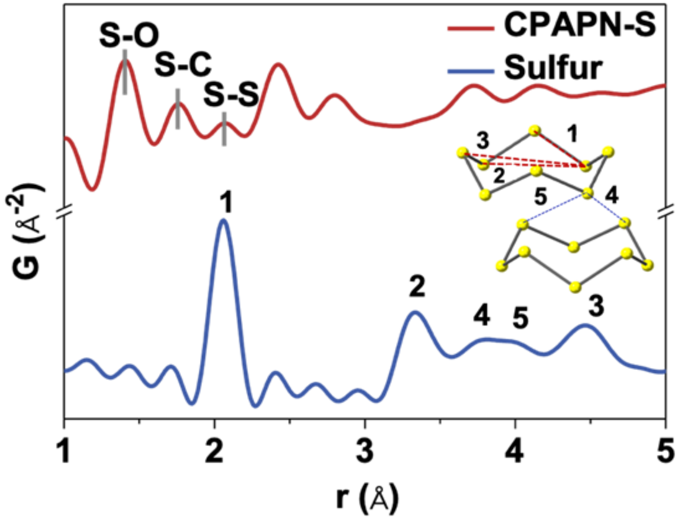
Team: P. Khalifah (BNL), J. Zhang (PNNL), M.S. Whittingham (Binghamton),Y.S. Meng (UCSD), R. Manithram (UT-Austin)

Chemistry of Materials, **32**, 1002-1010, “ACS Editor’s Choice”, Jan. 20, 2020, https://doi.org/10.1021/acs.chemmater.9b03646
Review of Scientific Instruments, **89**, 093002 (2018); https://doi.org/10.1063/1.5044555

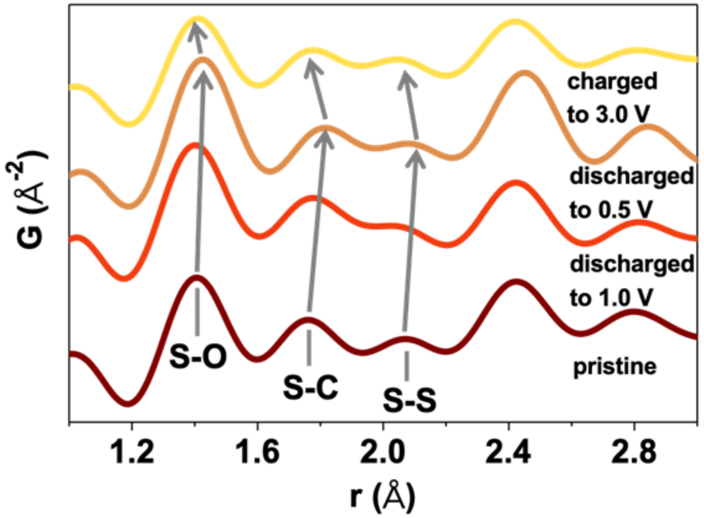
1b. Structural insights for carbon-sulfur hybrids



Ex situ reference data

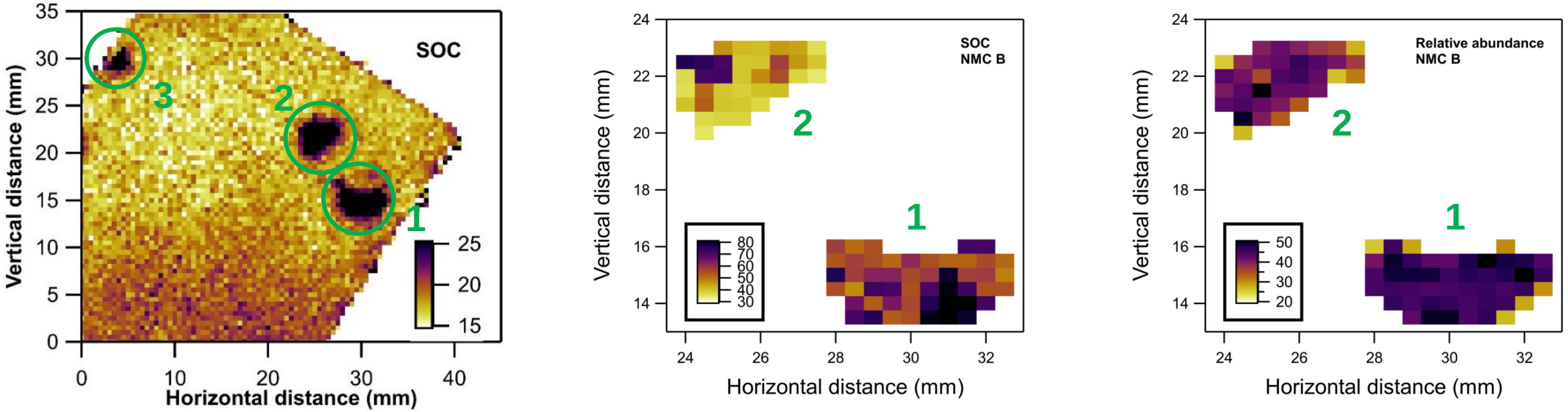


Operando cycling data



- Investigated polymeric carbon-oxygen-sulfur hybrids as alternatives to Li-S
- Bonding within hybrids was investigated by xPDF after synthesis and during cycling
  - Can independently resolve and characterize different sulfur bonds (S–O, S–C, and S–S)
- Inclusion of oxygen enhanced bonding of sulfides relative to carbon-only systems

2a. NMC pouch cell failure – diffraction mapping studies

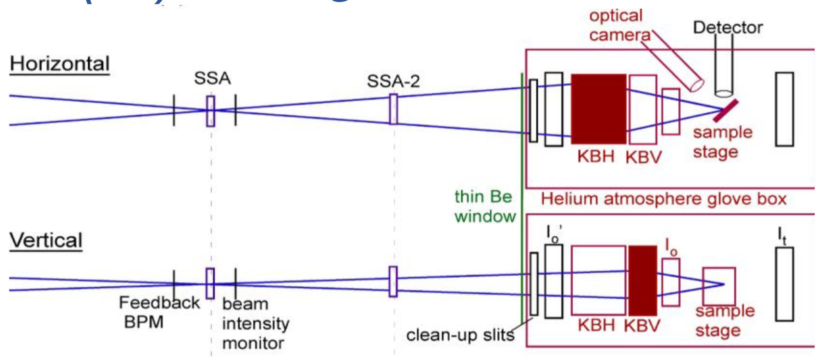


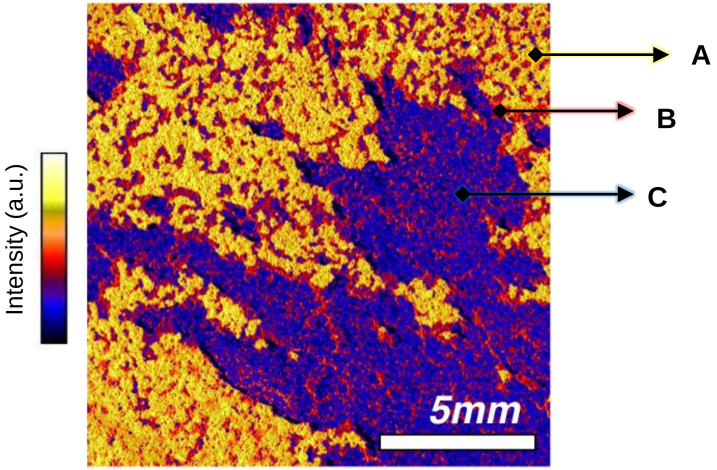
- Developed high-energy lateral mapping techniques for studying pouch cell inhomogeneity
  - Each map generated from the refinement of >5,000 high-energy powder diffraction patterns
- Applied to study cathode inhomogeneity in end-of-life NMC622/Li cell (after ~200 cycles)
- Observe “hot spots” in discharged EOL cell containing NMC with two distinct SOCs
  - Behavior of hot spots provides insights into the cell failure mechanism

Collaboration: P. Khalifah (BNL), J. Xiao (PNNL), E. Dufek (INL)

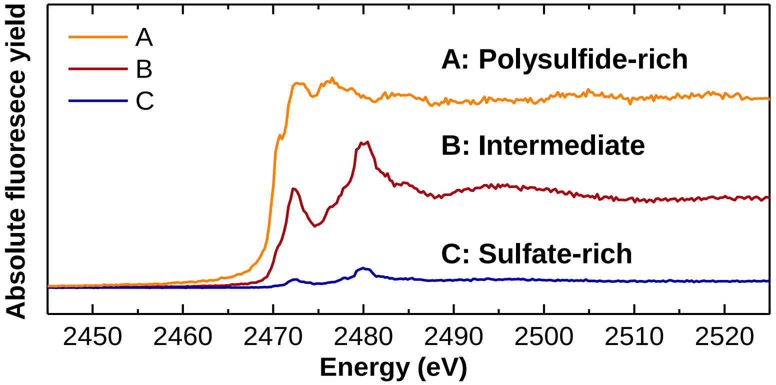
2a. (continued) XAS and XRF lateral mapping of Li-S cell

8-BM (TES) beamline @ NSLS-II





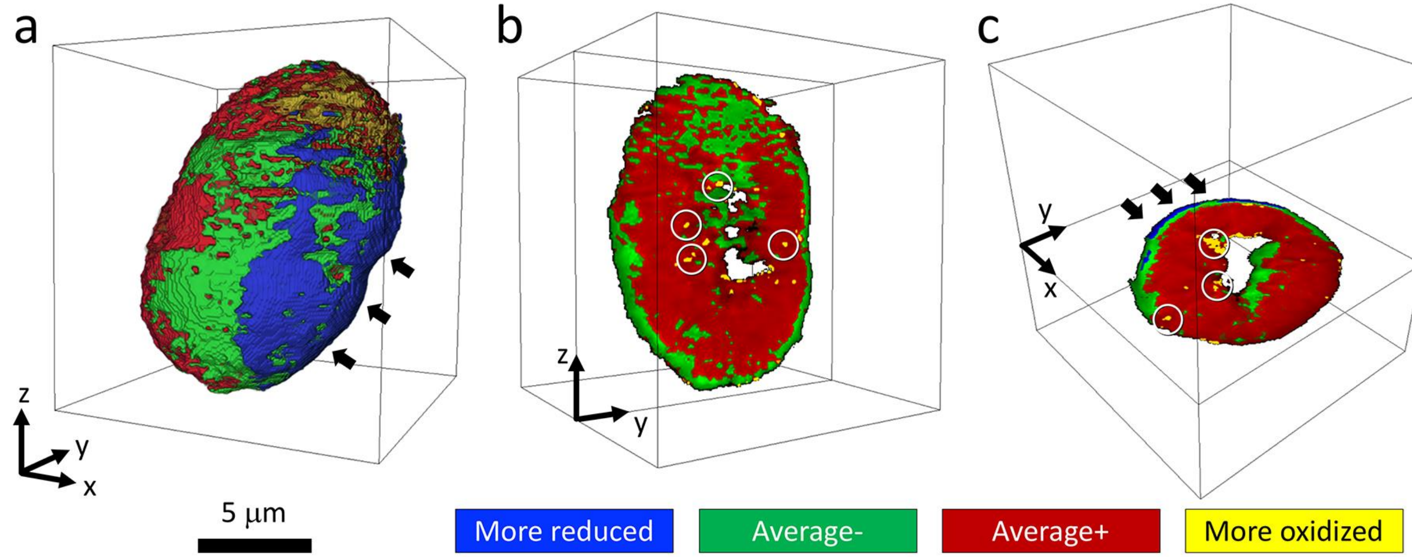
2D XRF image of S cathode (1.5 x 1.5 cm^2 area) at 2480 eV with 25 um pixel size

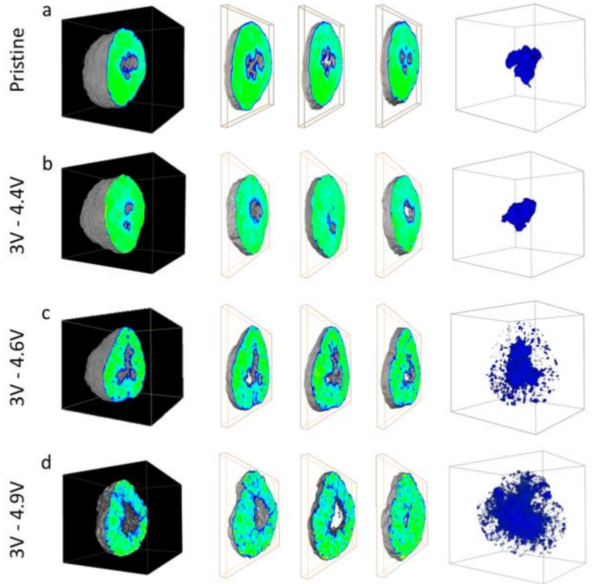


- Studied S speciation in Li-S cathode films with tender energy spectroscopy (TES)
- Sensitive to both crystalline and non-crystalline S species
  - Addresses the gap in sensitivity in conventional diffraction methods
- Observe macroscopic inhomogeneity in discharged Li-S film
  - Still working to resolve origin of this behavior

Collaboration: X. Yang (BNL), J. Xiao (PNNL), D. Lu (PNNL), and J. Liu (PNNL)

2b. Failure probed at single-particle level

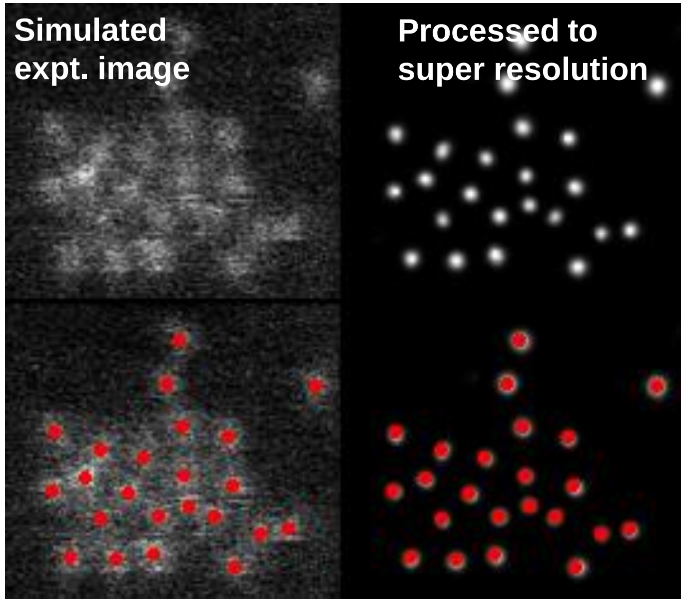




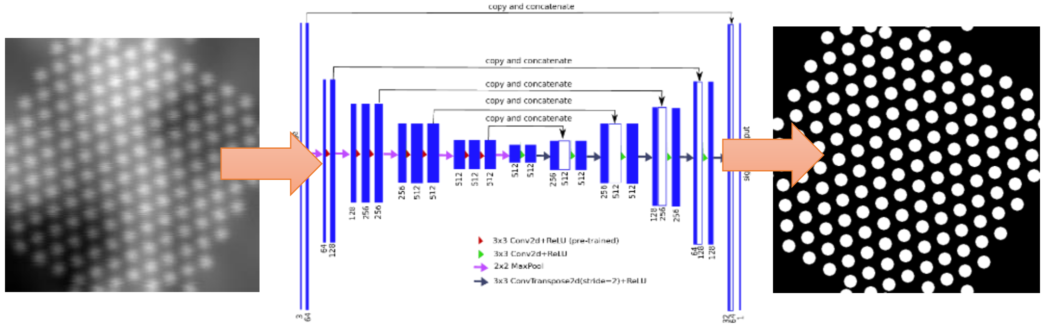
- Charging NMC622 to higher voltages leads to more rapid failure – what is origin?
- SOC inhomogeneity in single particles probed by TXM spectro-microscopy at SSRL
- Large differences in SOC after charge to 4.9V produces strain that causes cracking
  - Data and modeling suggests that strain is mitigated by hollow particles; lower cutoff voltage

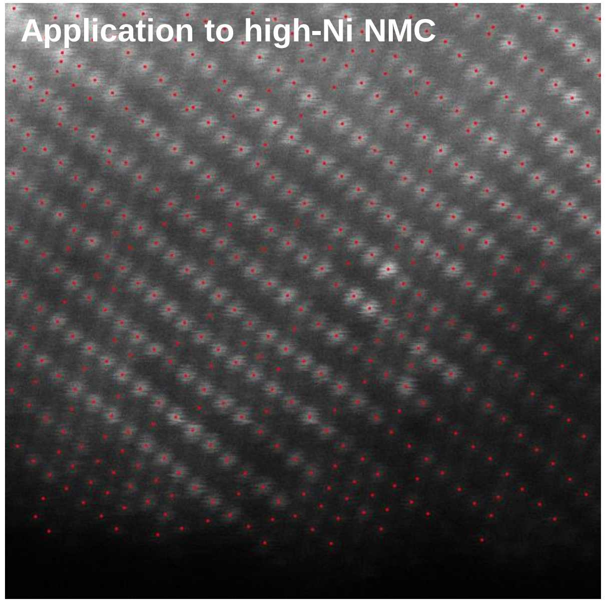
Collaboration: X.-Q. Yang (BNL), Y. Liu (SLAC), and R. Manithram (UT-Austin)

2c. Super-resolution EM imaging enabled by AI/ML



Convolutional Neural Net (Unet, Gen 1)





- Used BNL's GPU clusters to train deep convolutional neural networks to find atoms
  - Can provide sensitivity to atomic sites exceeding that of human eye
  - Enables low-dose imaging, allowing samples to be studied with minimal beam damage
- Starting to apply technique to track site mixing in high-Ni NMC compounds

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Collaboration X.-Q Yang (BNL), H. Xin (UCI), and J. Xiao (PNNL)

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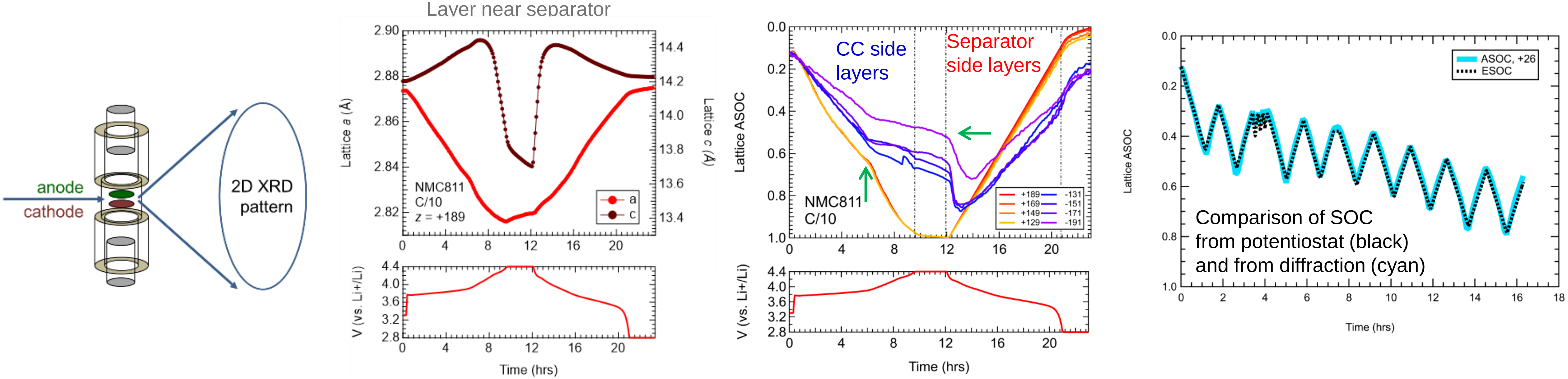
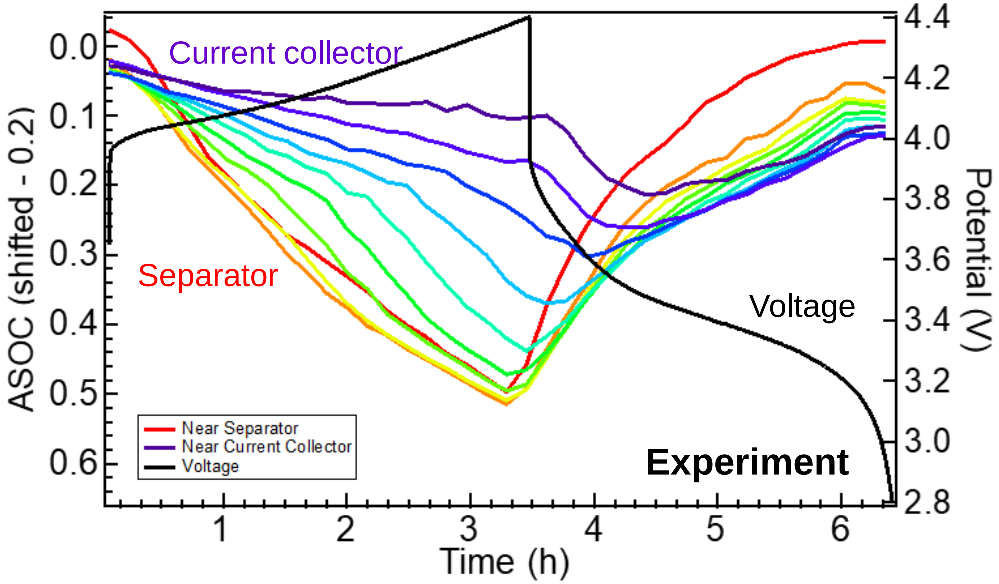
3a. Thick electrodes studied by depth profiling

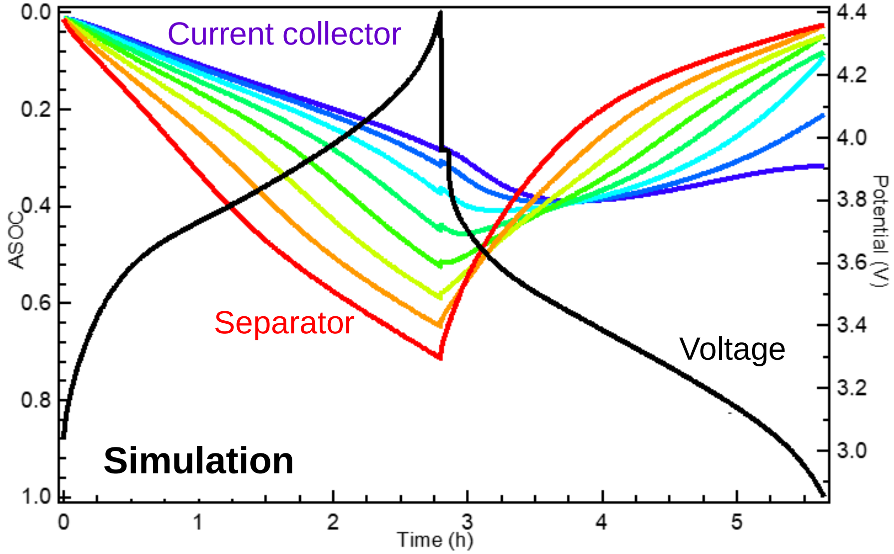


- Thick electrodes enable higher energy densities, but have larger SOC inhomogeneity
- Depth-dependent SOC determined through operando cycling measurements
  - Synchrotron data enable excellent spatial (10 – 20 μm) and temporal (5 min) resolution
- Observe a variety of unexpected behavior (e.g., SOC increasing during discharge)
  - Can these phenomena be captured by cell models? (w/ V. Submramanian, UT-Austin)

Collaboration: P. Khalifah (BNL), X.-Q. Yang (BNL), P. Liu (UCSD), K. Chapman (ANL), V. Subramanian (UT-Austin)

3a. Thick electrodes studied by depth profiling





- Parameterizing models that can reproduce observed behavior
  - Parameterizing based on complex multi-dimensional data, not just on simple voltage curve
  - Models that can fit time- and depth-dependent SOC will necessarily be predictive
- Models will be utilized to design thick electrode cells with optimal performance
  - Goal of maximizing delivered capacity and rate performance; predictions can be validated

Collaboration: P. Khalifah (BNL), X.-Q. Yang (BNL), P. Liu (UCSD), K. Chapman (ANL), V. Subramanian (UT-Austin)

Response to last year’s reviewer comments

- This project was not reviewed last year

Collaborations with other institutions

- ANL (Shin)
  - High-Ni NMC materials with concentration gradients
- Binghamton University (M.S. Whittingham)
  - High-Ni NMC materials and analysis
- INL (E. Dufek, B. Li)
  - Electrochemical evaluation of cells; well-characterized samples for *ex situ* and *operando* studies
- PNNL (J. Zhang, J. Xiao, D. Lu)
  - High-Ni NMC samples and analysis, NMC cathode films and pouch cells, Li-S electrodes and cells
- SLAC (Y. Liu)
  - TXM studies on high-Ni NMC
- UT-Austin (A. Manithram)
  - High-Ni NMC materials and analysis
- U. Maryland – College Park (C. Wang)
  - High sulfur loading S cathode material synthesized by carbonizing oxygen-rich PTCDA and nitrogen-rich PAN with sulfur (SPAN)
- UCSD (P. Liu, Y.S. Meng)
  - High-Ni NMC materials and analysis, thick films for depth profiling analysis, first-cycle capacity loss studies

Remaining challenges and barriers

- N/A

Proposed future research

- Extend lateral mapping and depth profiling methods to Li-S cells

- Resolve effects of annealing on NMC anti-site defect concentrations
- Quantify NMC local distortions and their effect on performance

- Investigate failure mechanisms for very Ni-rich NC and NCA samples
- Structural transitions and degradation pathways of very Ni-rich phases

Any proposed future work is subject to change based on funding levels

Summary

- Advanced characterization methods designed to meet B500 needs
    1. Material selection   2. Failure mechanisms   3. Predictive whole-cell models

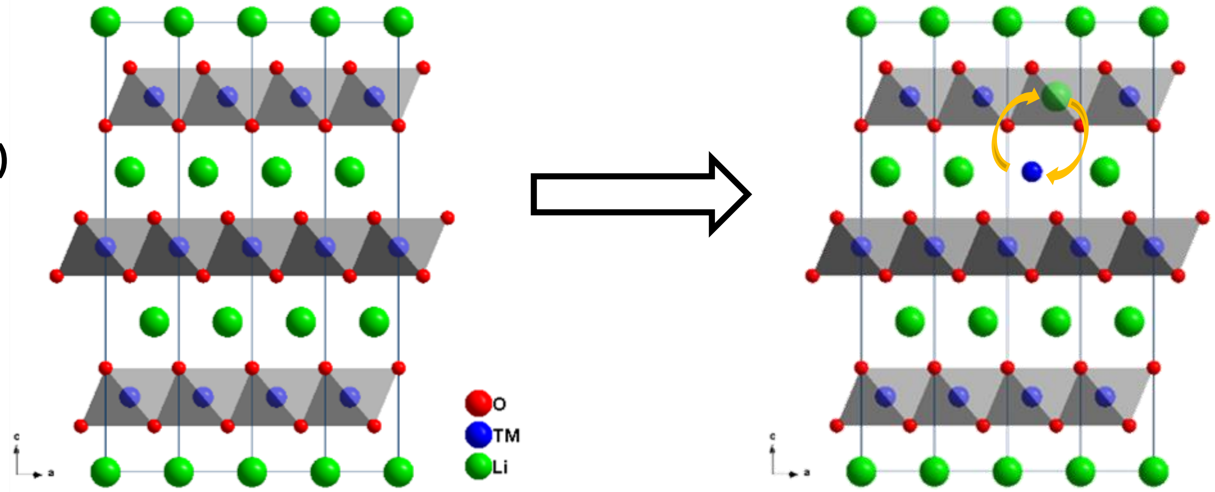
- Able to follow synthesis- and cycling-induced changes on many levels
    - Material, particle, electrode, and whole cell
    - Enabling fitting & modeling that can provide mechanistic & predictive insights

- Exceptional sensitivity achieved with novel approaches
    - Powder diffraction quantification of defects with unprecedent sensitivity
    - Used NNs to greatly enhanced sensitivity of EM to atomic defects
    - Elucidating both vertical and lateral inhomogeneity in NMC and sulfur cathodes

Technical back-up slides

Expected influence of defects on NMC properties

Ideal R-3m structure (α-$NaFeO_2$)



Paired anti-site defects (Ni_{Li} & Li_{Ni})

- In ideal NMC structure, ionic transport is 2D and electronic transport is 2D
  - Increasing dimensionality should improve performance
- Addition of paired anti-site defects (PAS) enables 3D ionic and electronic transport
  - Small amounts of PAS defects (2 – 5%) present in typical NMCs
  - Large amounts of PAS defects (>10%) known to adversely affect performance
  - For a given composition, optimal PAS defect concentration is unknown but can now be studied